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A Mathematical Model for Prediction of Physical Properties of the Coke Oven Charge During Carbonisation

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ABSTRACT

Mathematical models for the prediction of physical properties of the charge (e.g specific heat, density, and thermal conductivity) and heat of reaction during thermal decomposition of coal to coke have been constructed in terms of the changes in the chemical composition and structure. For realistic quantification of thermal transport processes in the oven , it is essential to predict the physical properties of the charge as they evolve during the carbonisation process. The models are based on the predictive procedure developed to address volatile matter evolution during carbonisation from knowledge of coal proximate analysis, ultimate analysis and heating profile. A first principle based formalism has been adopted to predict the physical properties of the charge and heat of carbonisation reaction as a function of the charge temperature during carbonisation supported with pertinent data. The predictions have been validated with published data, wherever possible. The models of physical properties are expected to generate critical temperature dependent property data of the oven charge, which would be vital for further development of a rigorous oven heat transfer model during carbonisation.

Key words: Process modelling, coke oven, physical properties, volatile evolution, carbonisation, heat of reaction

1. INTRODUCTION

Coal is destructively distilled in coke ovens to produce coke, and several by-products such as tar, ammonia high molecular weight hydrocarbons and coke oven gas. The blast furnace is to date the prime mover for pig iron production, which uses, besides other raw materials such as sinter and iron ore, coke for the purpose of reduction of oxides. Almost 500 kg of coke is consumed per ton of pig iron produced, and hence it is vital to integrate coke ovens with blast furnace production facilities. The coke produced has to meet stringent quality requirements, as it must withstand heavy burden load at high temperature inside the furnace. It is the only material inside the blast furnace which remains solid at temperatures of the order of 1773K, and supports the weight of other burden materials which react and melt. Some critical tests e.g. CRI (coke reactivity index) and CSR (coke strength after reaction) are conducted to ensure that the blast furnace is supplied with quality coke. As the coke moves on belt conveyors and undergoes several drops during transfer the Micum index test is also performed to ensure that it has requisite abrasion and impact resistance . Although most coke ovens used today are of the top charge type, there is an increasing tendency to adopt the stamp charge design. This is due to the fact that good quality coking coal is fast depleting world-wide, necessitating pre-treatment by stamping moist

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coal particles in a specially designed stamp-charge machine to provide high bulk density and uniform carbonisation inside the oven. In countries like India, where there is a dearth of quality coking coal, some steel plants have adopted this technology in which indigenous coal is blended with quality imported coking coal .

2. COKE OVEN CARBONISATION

The basic flowsheet of the carbonisation process during coke making has remained unchanged for almost a century. Coal is crushed so that about 80% of particles are less than 3 mm in diameter. It is then either charged from the top or stamp charged using stamp-charging and pushing (SCP) machine into slot-type ovens. A battery can contain several ovens usually 54 to 72 in number. The ovens, made of silica refractory brick, are of vertical slot type and are heated indirectly through the sidewalls. Between the walls of adjacent ovens are flues through which the combustion products of the fuel gas pass, maintaining the oven wall at a temperature in the range 1373K to 1573 K. Figure 1 shows a schematic of a coke oven battery for coke making operation.

The charge temperature history is of significant importance, together with the stages of carbonisation. Heat in the oven is transferred from the flue chamber through oven walls to the coal mass which gets heated rapidly, layer-wise with the evolution of moisture which escapes through the outlets at the top of the oven. Coking coals generally volatilise between 623 and 673 K and tar, ammonia and coke oven gas are generated at still higher temperatures. Layers of coke, semi-coke, coking front (plastic zone) , dry and moist coal occur in the oven from the wall inwards until the end of the carbonisation stage, which concludes when the centre mass temperature reaches about 1200 K. The plastic zone is impermeable and the gas generated in the un-reacted mass tends to bulge this layer resulting in stresses on the walls, which in extreme cases may be damaged. At a certain temperature, shrinkage occurs in both the width and height directions of the oven, fissures form in the surface layers of coke and general porosity exists in the interior coke cake. The total carbonisation cycle lasts about 18 to 20 hours, after which the coke is pushed out and quenched to ambient temperature, sized and stored.

The coking process is thermally driven /1-4/ and, therefore, accurate characterisation of heat transfer is fundamental to the development of any successful carbonisation model for the coke oven. The transfer of heat from the oven walls to the interior of the charge results in large temperature gradients. During coking, the temperature history of the charge can affect the plastic properties of the coal and severity of the contraction strains, which cause cracks and fissuration, both of which in turn affect the coke quality.

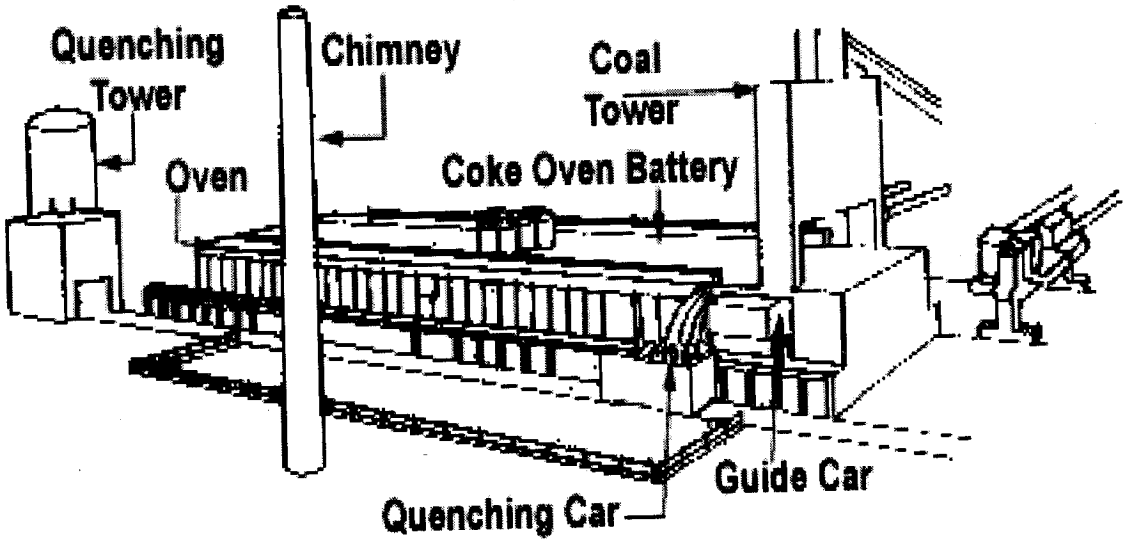

Fig. 1: Schematic of a typical coke oven battery

Furthermore, the energy consumption and the productivity (i.e. throughput) of the oven are also related to the charge temperature history. Many factors can distort the heating process; for example, uneven heat transfer from the flues can impose a significant vertical temperature gradient on the charge and result in coke of non-uniform quality. Even with uniform heating from oven walls, certain processes occurring within the charge (gas flow irregularities or re-condensation of free moisture, which has boiled elsewhere within the oven) may distort heating patterns in some parts of the oven and result in an non-uniform product. Figure 2 shows a schematic of intermediate stages of coking process in a coke oven.

Although the coking process described above is a highly developed technology, there are several incentives to modify traditional practice. These include:

a) Widening the range of coals used in coking blends so that economical supplies can be maintained as reserves of prime coking coal are depleted.
b) Changing oven operational practices to improve coke quality (or to maintaining coke quality when inherently less suitable coals or blends are used).
c) Increasing oven productivity.
d) Reducing energy consumption.

The objective of this study is the formulation of models describing the main chemical and physical changes occurring during thermal decomposition of coal and, as a consequence, development of a computational procedure to predict the processes of de-volatilisation and change in composition of the charge which can be used to construct models for predicting physical properties of the charge. The models relating to physical

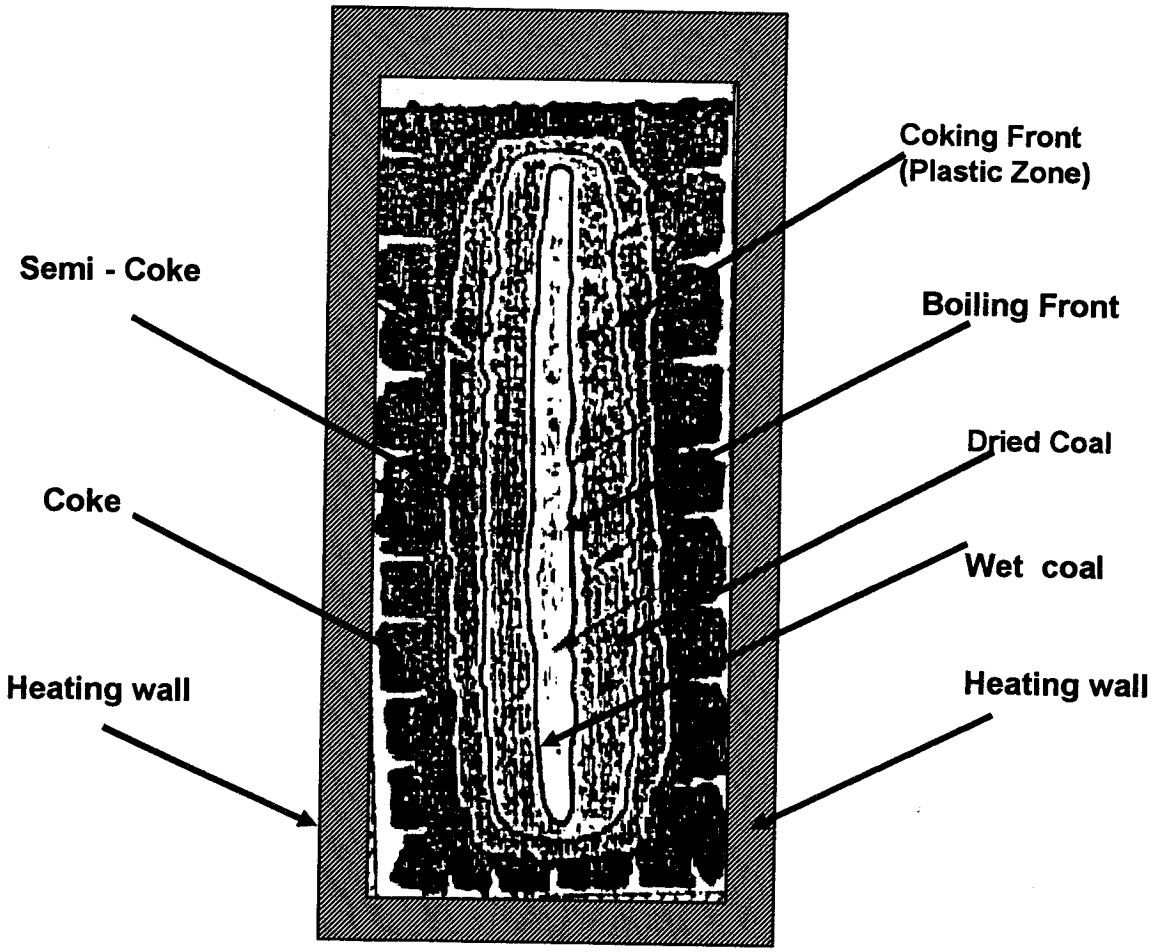

Fig.2: Conditions within coke oven during intermediate stages of coking process

properties of the charge (bulk density, specific heat, thermal conductivity) and heat of carbonisation reaction during complete coking cycle have been developed on the basis of the above model.

3. ANALYTICAL MODELLING APPROACH

The thermal behaviour of stationary packed beds of granular material is a problem of frequent interest in the processing of materials. However, the particular task of determining the response of the charge with temperature dependent properties within the individual oven of a coke oven battery to heating from the adjacent flues is rendered especially difficult by the associated phenomena, which must be taken into account. The predominant processes are: (1) evolution of volatile matter and change of composition of the charge during carbonisation, (2) thermo-physical properties which are strongly dependent on local temperature, (3) various exothermic and endothermic processes, particularly phase changes and structural rearrangements, which act as sources or sinks of energy. Because of the variety of processes involved and the transient, multi-dimensional nature of the problem, attempts to model commercial coke making process are somewhat scarce and challenging /1-4,5,6/.

3.1 Model for volatile matter evolution

Models of the thermo-physical properties of the charge during carbonisation in the stamp-charged coke ovens critically depend on the composition and yield of the charge and volatile matter evolution during the coking cycle to be known *a priori.* Provided that the composition and rate of evolution of each of the volatile matter species can be predicted, the mass and composition of the charge can be calculated from that of the coal by mass balance. This methodology forms the basis of the present model. For keeping the analysis mathematically tractable, only the compositions of the coal / blend in terms of carbon, hydrogen, oxygen, nitrogen and sulphur is considered. Other elements are known to occur in coal, but amount to less than 0.3% and are therefore, ignored. The composition on the basis of ultimate analysis for typical coals used in Indian steel works has been used in this study.

The kinetics of volatile matter release can be described by a system of parallel first-order reactions/5,6,/ for which the rate constants vary with temperature according to Arrhenius relationship in a generalised framework.

$$\frac{d\delta}{dt} = \left[\kappa \exp(-E/RT)\right] (1 - \delta) \qquad (1)$$

where δ is the fraction of the component of volatile matter released during time t, κ is the frequency factor, E is the activation energy, R is the universal gas constant and T is temperature in Kelvin (K). Each of the volatile matter species is subdivided into components corresponding to different activation energies and the release of each of these components is described by equation (1). The activation energies /1/ for the volatile matter species do not, in general, correspond to Gaussian distribution; therefore, a transformed Rossin-Rammler function is used instead to describe the distribution /1/.

$$F_j(E) = \exp\{-((E - E_0)/\varepsilon)^{\beta}\}; (j = 1,N) \qquad (2)$$

where E_0 is the starting activation energy, ε and β vary both with species and coal rank and N is the number of species considered in the volatile matter. For the j^{th} volatile matter species, the cumulative amount m_j expressed as a fraction of dry ash free (daf) coal released at a time t is given by

$$m_j(t) = \overline{m_j} \int_0^1 \delta(t,E)\, dF_j(E)\, dE = -\overline{m_j} \int_{E_o}^{\infty} \delta(t,E) \frac{dF_j(E)}{dE} dE \; ; \; (j=1,2 \ldots N) \qquad (3)$$

where $\overline{m_j}$ are the final yields (as mass fraction of daf coal) of coke for the j^{th} species.

Therefore, the rate of release of species is given by

$$\frac{dm_j}{dt} = \overline{m_j} \int_0^{\infty} \frac{\partial \delta}{\partial t} \frac{dF_j(E)}{dE} dE \; ; \; (j = 1,2 \ldots N) \qquad (4)$$

Equations (3) and (4) can be solved using an appropriate numerical method to predict the kinetics of

release of the number of volatile matter species considered in the model.

The cumulative masses of the volatile matter species, m_j (t), $j=1...N$, at time t calculated from equation (3) is used to determine the mass of char remaining at time t, m_o (t) by an overall mass balance

$$m_o(t) = 1 - \sum_{j=1}^{N} m_j(t) \qquad (5)$$

Element balances can be used to calculate the composition of the char residues at time t and the details are available in the published literature /6,7/.

3.2 Models for prediction of physical properties of the charge

The development of general mathematical models to describe changes of thermo-physical properties of coal during carbonisation has received little attention, in spite of the importance of these parameters in understanding and describing the thermal processes of coal during carbonisation. Any comprehensive heat transfer model of coke oven requires appropriate sub-models to evaluate physical properties of the charge, such as bulk density, specific heat, effective thermal conductivity and heats of reactions during carbonisation towards the final stages of carbonisation cycle, i.e beyond 973 K. In order to provide estimates for the wide range of conditions which can occur in a coke oven, a series of mechanistic models based on fundamental principles and pertinent published data have been developed.

The models of the physical property prediction are based on the yield and composition of the char residue and can, therefore be linked to the kinetic model of volatile matter evolution. In general, changes in the physical properties during carbonisation are thought to result from the chemical changes occurring, though in some cases (e.g. specific heat and thermal conductivity) temperature may also be an independent variable. The models for thermo-physical properties are based on changes in chemical composition predicted by the kinetic model of volatile matter evolution. This enables the thermo-physical properties during carbonisation to be related to the composition of the initial coal and heating condition. A brief description of the formalism is presented below.

(A) Bulk Density:

Increase in bulk density is sought to improve coke quality and oven throughput. For a wet charge, the bulk density can be increased by stamp charging. Drying and preheating the coal to 323 K before charging the oven also results in an increase in the bulk density (dry basis), typically by about 10 %.

The loss of volatile matter reduces the average bulk density of the charge, although some shrinkage also occurs during carbonisation. The bulk density, γ, of an element of charge is given by

$$\gamma = \gamma_0 Y / (1+\Delta V) \qquad (6)$$

where γ_0 is the initial (wet) bulk density of the charge, Y is the yield of the coke (per mass of initial charge) and ΔV is the fractional volume changes of the charge ($\Delta V<0$ implies shrinkage). The charge shrinks progressively during carbonisation. Because the shrinkage is small, the approximation of using a constant value throughout carbonisation is made in this model. It is also assumed, in the absence of extensive experimental data, that the internal shrinkage normal to the walls and doors is negligible. The analytical details pertaining to evaluation of the bulk density of particulate solid is described elsewhere /7-9/. The methodology and some pertinent data have been utilized to evaluate the charge bulk density as a function of coking temperature.

(B) Heat of Reactions:

It is often observed that the centre of an oven charge becomes hotter than the wall towards the end of carbonisation, indicating the existence of endothermic reaction. Heat balance on a coke oven shows that the net effect of the reactions is to provide approximately 15 – 20 % of the total heat required for carbonisation (equivalent to 0.45 MJ /KG initial coal basis at ambient temperature, i.e excluding enthalpy changes). Heats of reactions of this magnitude will clearly have a significant effect on the temperature history of the coke oven charge. The heats of exothermic reactions during carbonisation /8,9/ can be given by the following

equation for the rate of release of heat (dq/dt) under isothermal conditions at temperature T K

$$\frac{dq}{dt} + \sum_{j=0}^{N} \frac{d}{dt}(u_j m_j) = 0 \qquad (7)$$

where q is the heat release, daf coal basis, u_j , (j = 0,1,2...N), are heats of formation at temperature T and m_j , (J= 0, 1,2.....N), are the mass fractions of carbonisation products daf coal basis. The index, j = 0,1...N+1 refers to char and the volatile matter species considered in the model of volatile matter evolution. The heats of formation at temperature T K for the volatile matter species is approximated by a quadratic function of temperature /7-10/:

$$u_j = \sum_{k=0}^{2} P_{jk} T^K \qquad (8)$$

The coefficients P_{jk} are derived from standard tables of physical and chemical properties /9,10/. For the char the heat of formation is calculated from the standard heat of combustion using Hess and Kirchoff law /11-14/:

$$u_o = H - \sum_{i=1}^{5} \phi_i y_i + \Delta h \qquad (9)$$

where H= Heat of combustion at 298 K, ϕi (i=1...5) are constants representing the heats of combustion of elements C, H, O, N and S, respectively (at 298 K) and Δh is the change in enthalpy from 298 to T K. The values of the coefficients ϕ_i are available in the standard tables. The correlation, as cited in the literature /7,8/ has been used to evaluate heats of combustion of coal and coke in terms of their ultimate analysis.

$$H = \sum_{i=1}^{5} \lambda_i y_i \qquad (10)$$

where y_i is the mass fractions of element 'i' on daf basis, and each λ_i is a known constant /7,/. The enthalpy changes from 298 to T K for the coal, char or coke are given as:

$$\Delta h = \sum_{i=1}^{5} (y_i / \mu_i) f(\bar{T}) \qquad (11)$$

and μ_i is the respective atomic weight of the element 'i' /7- 9/

$$f(\bar{T}) = R(380\, g_o (380/\bar{T}) + 3600\, g_o (1800/\bar{T}) - 156) \qquad (12)$$

Using equations (7) – (12), the rate equation for heat release can be expressed as:

$$\frac{dq}{dt} + \sum_{i=1}^{5} (\lambda_i - \phi_i + f(\bar{T})/\mu_i) \frac{d}{dt}(m_o y_i) + \sum_{j=1}^{N} \left(\sum_{k=0}^{2} P_{jk} T^k\right) \frac{dm_j}{dt} = 0 \qquad (13)$$

The heat release can also be expressed in terms of volatiles release rate in the following form:

$$\frac{dq}{dt} = \sum_{j=1}^{N} \frac{\partial q}{\partial m_j} \frac{dm_j}{dt} \qquad (14)$$

where

$$\frac{dq}{dt} = \sum_{i=1}^{5} A_{ij} (\lambda_i - \phi_i + f(\bar{T})/\mu) - \sum_{K=0}^{2} P_{jK} T^K \qquad (15)$$

(C) Specific Heat:

The Dulong and Petit law states that the specific heat of a substance may be calculated as 3R J/Kg-atom-K, where R is the gas constant (8314.4 J / Kmol –K). This law is found to be approximately true for many substances at ambient temperature, although in some cases the value 3R J/Kg-atom-K is approached only at elevated temperatures. Classical statistical mechanics provides a theoretical interpretation of Dulong & Petit law. The principle of equipartition of energy states that the mean energy associated with each degrees of freedom of the molecule is the same, and is proportional to temperature. For a solid, each atom is able to oscillate independently in each of the three dimensions, but there

is no translational and rotational energy. In practice, this represents the maximum attainable specific heat because quantum effects prevent the vibrational modes becoming fully excited at low temperatures.

It was not until the development of quantum theory that a satisfactory explanation for the temperature dependence of specific heat was found. Subsequently, Debye developed a model which allowed for a distribution of oscillation frequencies corresponding to the propagation of sound waves in a continuum. This permitted more accurate description of specific heats , particularly near absolute zero.

$$c = 3rd(T_k/\theta_D) \tag{16}$$

where, θ_D is the characteristic Debye temperature of the solid and the function D is defined by /7,8/:

$$D(y) = 3y^3 \int_0^{1/y} v^4 e^v /(e^v - 1)^2 dv \tag{17}$$

The Debye function *D(y)* can be evaluated numerically using a higher order Runge-Kutta integration routine.

However, an attempt has been made to describe the variation in specific heats of coal and cokes with temperature using the most widely used Einstein model. The Einstein model of specific heat assumes that the atoms oscillate independently in three dimensions with a common characteristic frequency. The theory leads to the following expressions for the specific heat ./9, 10/.

$$C = 3R(E(T_K/\Theta_E) \tag{18}$$

where, Θ_E is the characteristic Einstein temperature of the solid (K), T_K is the temperature (K) and the function E (y) is the *Einstein function* for specific heat, defined as:

$$E(y) = e^{1/y}/(y(e^{1/y} - 1))^2 \tag{19}$$

Although Debye's specific heat model is equally or even more accurate, this has not been used in the present formulation because small improvements in accuracy of the temperatures of interest do not justify the extra computational complexity.

(D) Effective Thermal Conductivity:

It is assumed that that the main mechanism responsible for heat transfer in a coke oven charge can be described by an effective (overall) thermal conductivity comprising,

a) conduction through gas phase
b) conduction through the solid phase
c) radiation across interstices and pores
d) radiation across the cracks and fissures

The heat transfer coefficients for natural convection are usually small. This mechanism has therefore been excluded from the present study. In the early stages of carbonisation, a coke oven charge consists of coal particles surrounded by air or by the steam produced as the charge dries up. The thermal conductivity is low as heat transfer between particles relies largely on conduction across the gas film. The formation, during the plastic stage, of a continuous solid phase is therefore expected to increase the thermal conductivity. Without elaborating the intermediate mathematical steps, the final expression for effective thermal conductivity /11,12,15/ of the particulate charge is summarised by the following equation:

$$K_{part} = w_2 k_3 + (1-w_2)/(\varepsilon'/(k_1+k_2)+(1-\varepsilon')/k_0) \tag{20}$$

where, K_{part} is the overall effective thermal conductivity of the particulate charge; k_0, k_1, k_2 and k_3 are respectively contributions from solid conduction, gas conduction, radiation across the interstices and conduction through moisture and,

$$\varepsilon' = 1 - (1-\varepsilon)^{0.5} \tag{21}$$

where, ε is the total charge porosity.

Without elaborating the intermediate mathematical steps, which are available elsewhere, /11,12,15/, the final expression for the effective thermal conductivity of the coke charge is summarised by the following equation:

$$K_{coke} = (1-\varepsilon) k_0 + \varepsilon k_1 + \varepsilon_{int} k_2 + \varepsilon_{ext} k_2 \tag{22}$$

where K_{coke} is the overall effective thermal conductivity of the coke charge, ε is the total charge porosity; ε_{int} the

fraction of the charge volume occupied by internal pores; and ε_{ext} is the fraction of the charge volume occupied by the fissures and cracks.

For simplicity, the changeover from the particulate charge to coke charge is assumed to occur at the re-solidification temperature. Since the density and porosity calculations are based on the models for volatile matter evolution, the charge thermal conductivity is estimated from the proximate and ultimate analysis of coal, the initial bulk density and heating profile. The proximate and ultimate analysis of typical Indian coal used for carbonisation in integrated steel plant is mentioned in Table1. The data has been utilized for simulation runs to predict the physical properties and heat of reactions. The heating rate considered in this simulation is 3K /minute. The bulk densities of the stamp charged and top charged coals are 1150 and 750 Kg/m^3 respectively

Table I

Analysis of a typical Indian coking coal used in the steel plant

Proximate Analysis (mass %)					
	Ash	**VM**	**FC**		
Typical Indian coking coal	16.95	25.80	57.25		
Ultimate Analysis (dry ash free basis) mass %					
	C	**H**	**O**	**N**	**S**
Typical Indian coking coal	84.63	5.31	1.87	0.74	7.45

3.3 Numerical implementation

For implementation of the mathematical models, an in-house interactive FORTRAN code named ***COKESIM-1*** (Coke oven simulation-1) /16/ has been developed to solve the governing equations of the model numerically for constant heating rate conditions. After acquisition and preliminary processing of the input data for typical Indian coal used in steel works, the code calculates the final yields of primary volatile matter and secondary volatile matter on a dry ash free basis. The code then enters an iterative loop in which the temperature is increased from 623 K in steps as desired by the user. At each stage of iteration, the masses in primary volatile matter and the cumulative yields of the three secondary volatile matter species are revised. The semi-coke yield and composition are calculated by mass balance on the five elements present and used to predict the mean relative atomic mass of the semi coke.

The *COKESIM –1* code, which calculates the yields and composition of the volatile matter and semi-coke composition has been extended, using the models of physical properties to calculate the physical properties of the charge and heats of reaction during coke oven carbonisation. This extended in-house interactive FORTRAN code has been named as ***COKESIM-2*** (Coke oven simulation-2). The code requires as input, the ultimate analysis of the coal, the conditions of the coal as charged (i.e moisture, ash, bulk density, temperature etc,) and the heating rate (assumed constant). The code calculates all the required physical properties of the charge during carbonisation. The calculations are carried out in an iterative loop in which the temperature is increased at a constant rate. The calculation for each of the physical properties' models is based on the predictions of volatile matter evolution and temperature alone. The results can be printed at the end of each iteration. Execution of the program terminates when the temperature reaches the specified final value.

4. RESULTS AND DISCUSSION

As stated above, the calculations for each of the physical properties models are primarily based on the predictions of the volatile matter evolution model and temperature alone. Volatile matter evolution is described in the model by a system of parallel first order reactions governed by a distribution of activation energies. The predicted primary and secondary volatile matter yield (daf initial coal basis) are shown in Fig. 3 and Fig. 4, respectively. The predicted total yield of volatile matter (at heating rate of 3 K / min) is shown in Fig. 5. The evolution of primary volatile matter appears to be complete by 873 K, though the secondary volatile matter species continue to be released till 1273 K. The cumulative matter yield is validated with the Thermo-Gravimetric Analysis (TGA) experiments conducted by the investigators with the identical Indian coal sample and also with the experimental investigations published

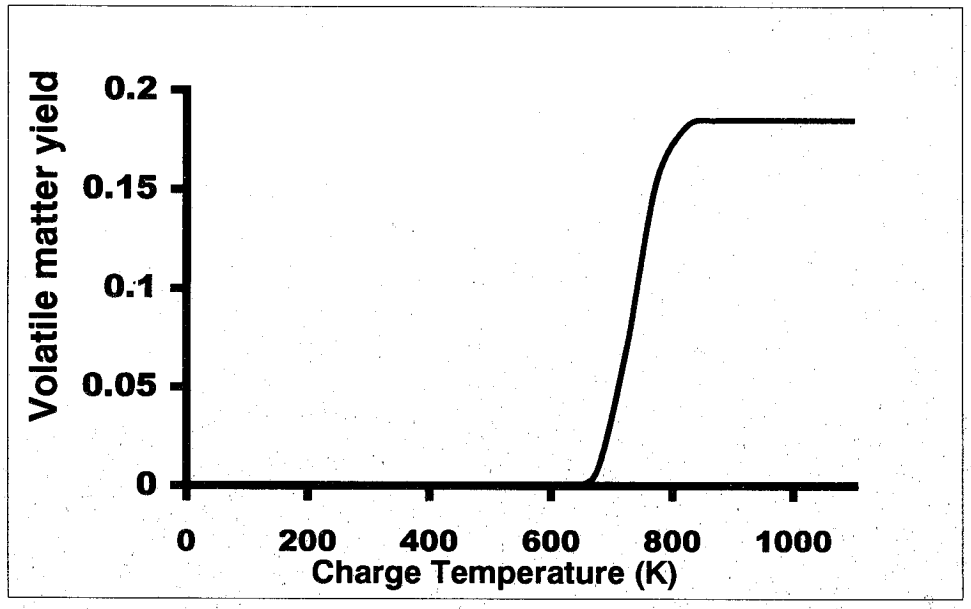

Fig.3: Model based prediction for primary volatile matter yield

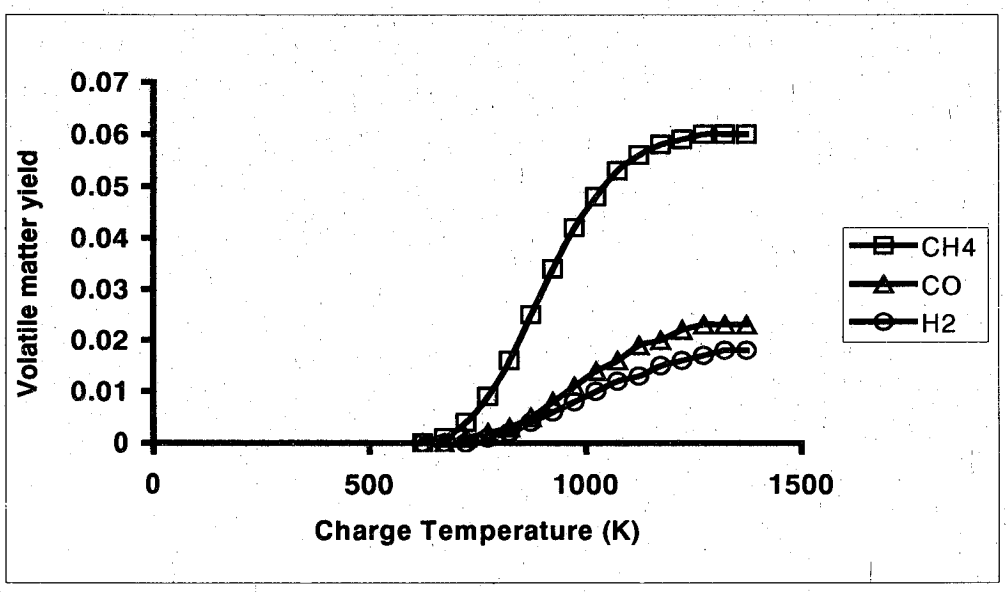

Fig.4: Model based prediction for secondary volatile matter yield

and widely referred to in the literature /6-9/ for top charged coke oven. Literature pertaining to stamp charged coke ovens are extremely scanty. In principle, the basic process phenomenology for both stamp charged and top charged batteries are intrinsically similar except variations in the bulk density and moisture content of the charge. Figure 6 shows the variation of carbon and hydrogen content of the charge as carbonisation process progresses. The predicted pattern of the total volatile matter release is in reasonable general agreement with that observed experimentally. In particular, the model reproduces the rapid evolution of primary volatile matter between 673 K and 773 K.

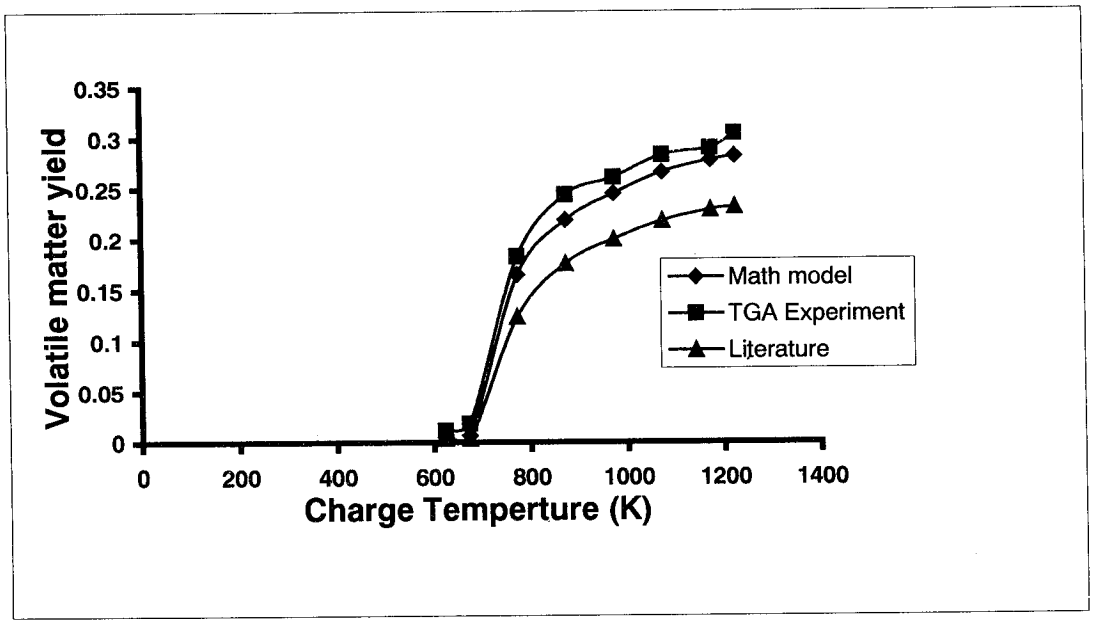

Fig.5: Predictions for total volatile matter yield

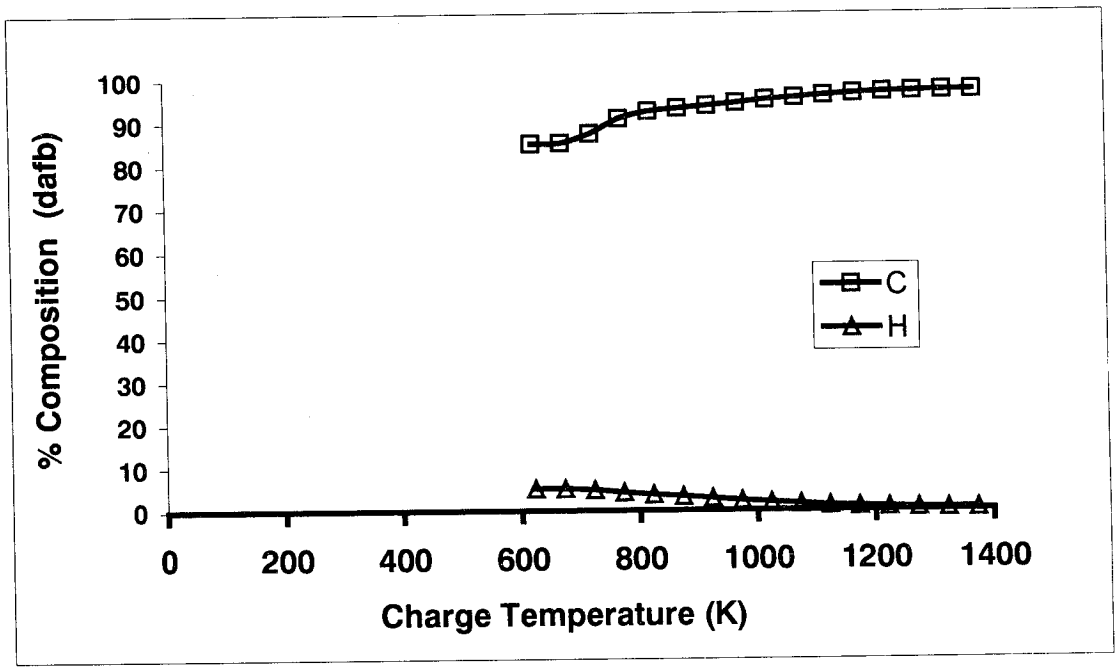

Fig.6: Model predictions for variation of charge composition

The evolution of three secondary volatile a matter species (CH_4, H_2, CO) occurs simultaneously. In Fig.4, the markers indicate the yield of different volatile species as predicted by the mathematical model. Although each may be the final product of a complex sequence of reactions, it is assumed in the model that their evolution can be considered independently.

Figure 7 shows that most of the exothermic heat release during carbonisation is predicted as occurring above 1073 K which is in agreement with the

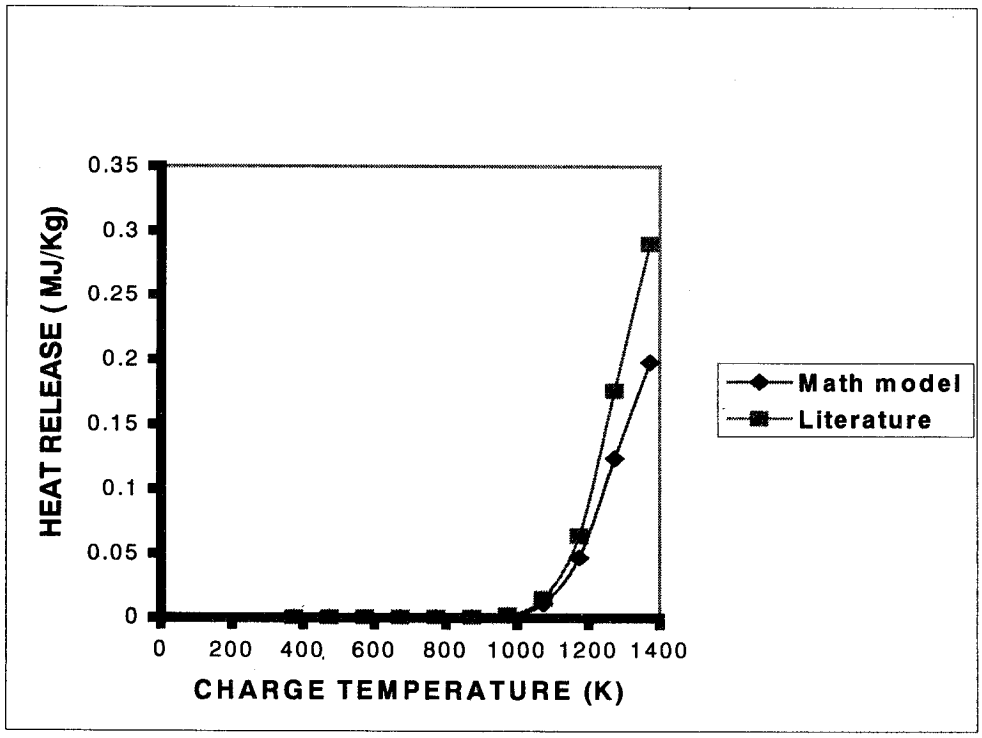

Fig. 7: Variation of carbonisation heat of reaction

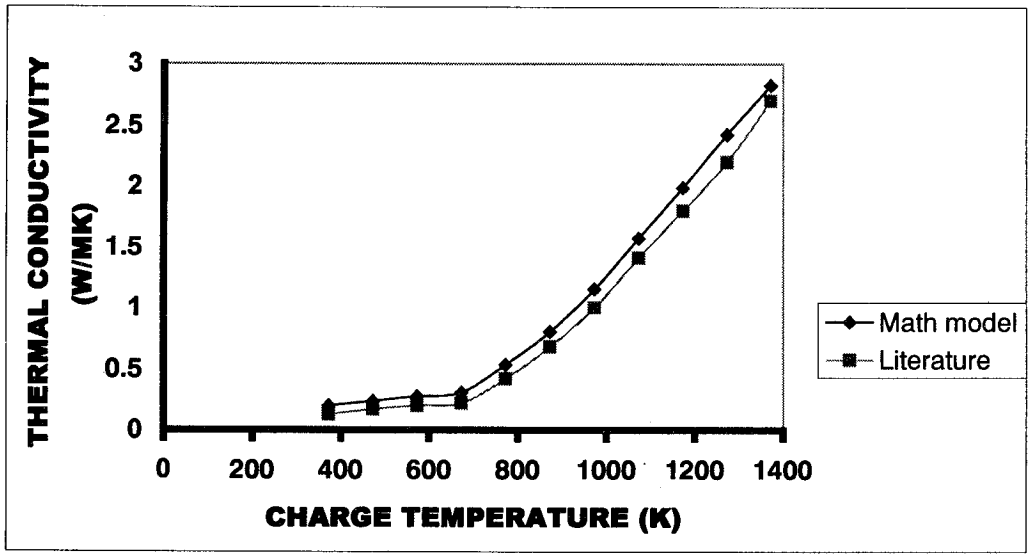

Fig.8: Variation of effective thermal conductivity

experimental observations cited in published literature /7,8/. The reactions responsible for the centre of a coke oven charge becoming hotter than the walls towards the end of carbonisation do occur at high temperature, which is consistent with the model predictions. The heat release does not occur, however, until the reactive intermediate semi-coke produced by the release of secondary volatile matter is converted into mature coke. Figure 8 shows the variation of effective (overall) thermal conductivity of the coke oven charge as a function of temperature. The thermal conductivity increases slowly up to 673 K then accelerates rapidly as

a function of temperature. The solid thermal conductivity increases slowly until decomposition begins, after which a rapid increase occurs until the thermal conductivity of mature coke is approached. The gas thermal conductivity also increases after the onset of volatile matter evolution because the thermal conductivity of hydrogen is considerably greater than that of the air or steam initially present. The effective thermal conductivity due to radiation increases as cube of the absolute temperature, while the heat flux increases as fourth power of absolute temperature. Solid conduction, gas conduction and radiation all contribute to the effective thermal conductivity of a coke oven charge. Gas conduction limits the rate of heat transfer during the particulate charge, whereas radiation along the fissures becomes the major mechanism in the final stages of carbonisation.

As shown in Fig. 9, the present model predicts a relatively rapid increase in specific heat between ambient temperature and 673 K, followed by a decrease between 773 and 1273 K. The existence of a maximum specific heat in the range 673 to 773 K is thought to be responsible for the apparent endothermic reactions occurring in this temperature range. In the case of 25 to 30 %, volatile matter coal, the decrease in the specific heat value from the maximum value to that at 1273 K is 13%. The initial increase in the specific heat is attributable to the effect of temperature alone. Once the decomposition begins, the specific heat increases asymptotically to the maximum value. The variation of specific heat with temperature has been described by Einstein's model along with composition by assuming that the vibrational energy at any temperature is the same for each atom. When used with the model of volatile matter evolution to predict the specific heat of the coal during carbonisation, it is found that the specific heat rises rapidly to a maximum value at 673 to 773 K, and subsequently to the Dulong & Petit /7/ limiting value for carbon at high temperature. The variation of the bulk density with the charge temperature is shown in Fig. 10. The predicted decrease in the bulk density during carbonisation occurs because of the mass loss resulting from volatile matter and the removal of moisture. The major changes in bulk density therefore occur at 373 K and during the primary volatile matter evolution stage. The shrinkage of the coke formed near the oven wall is likely to reduce the bulk density of the coke formed at the oven centre. This effect is, however, not taken into account in the present model, which calculates average bulk density of the

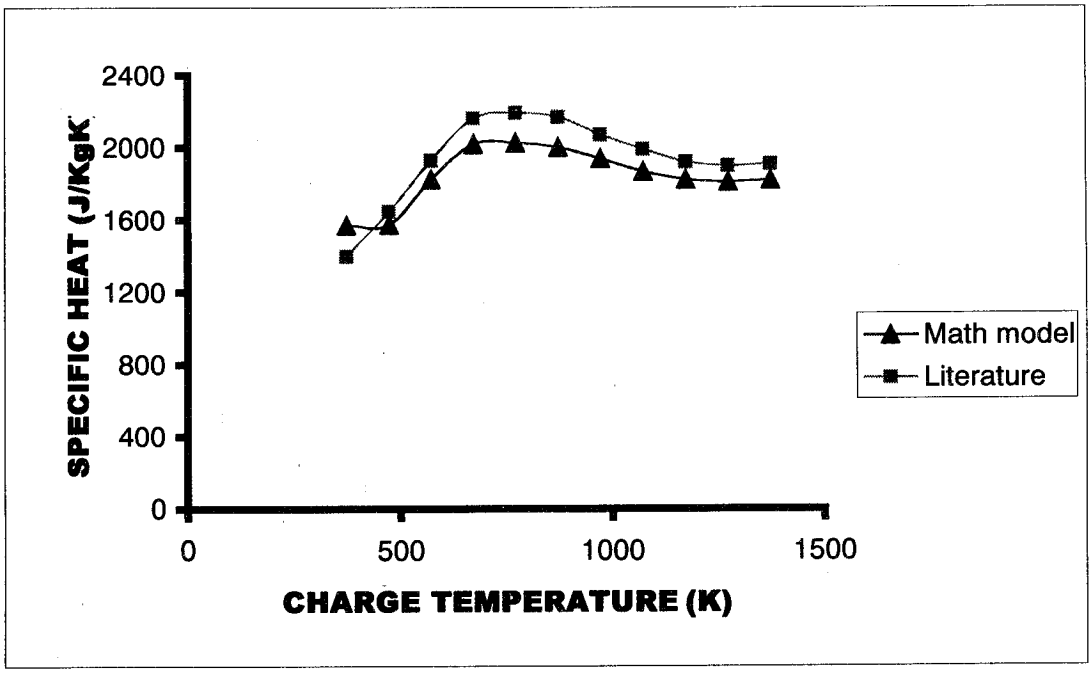

Fig. 9: Variation of specific heat with charge temperature

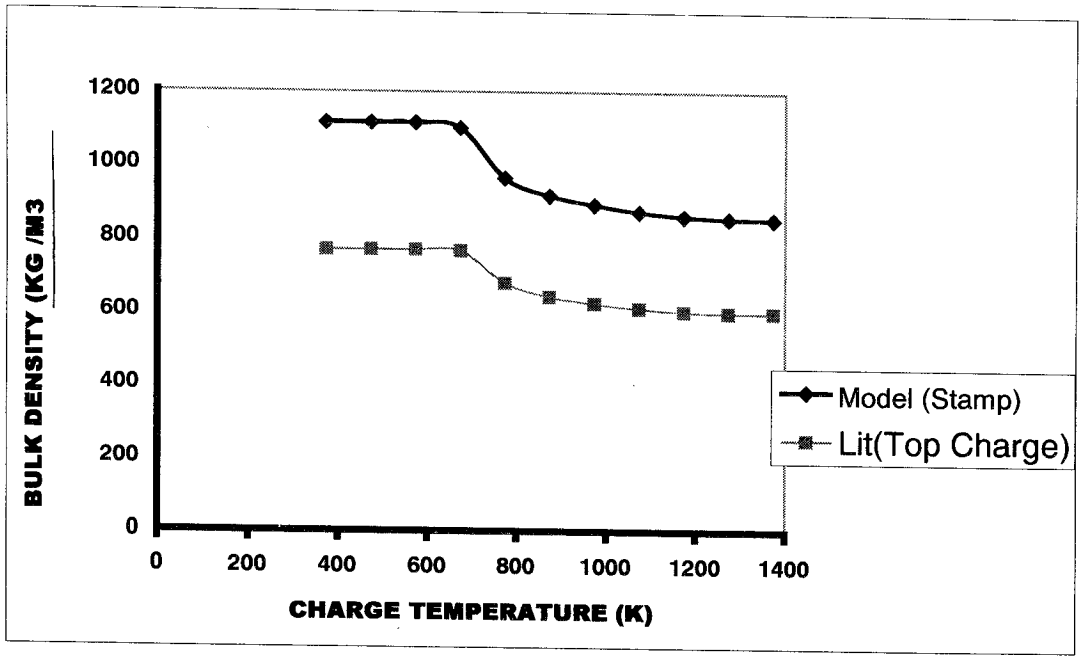

Fig.10: Variation of bulk density with charge temperature

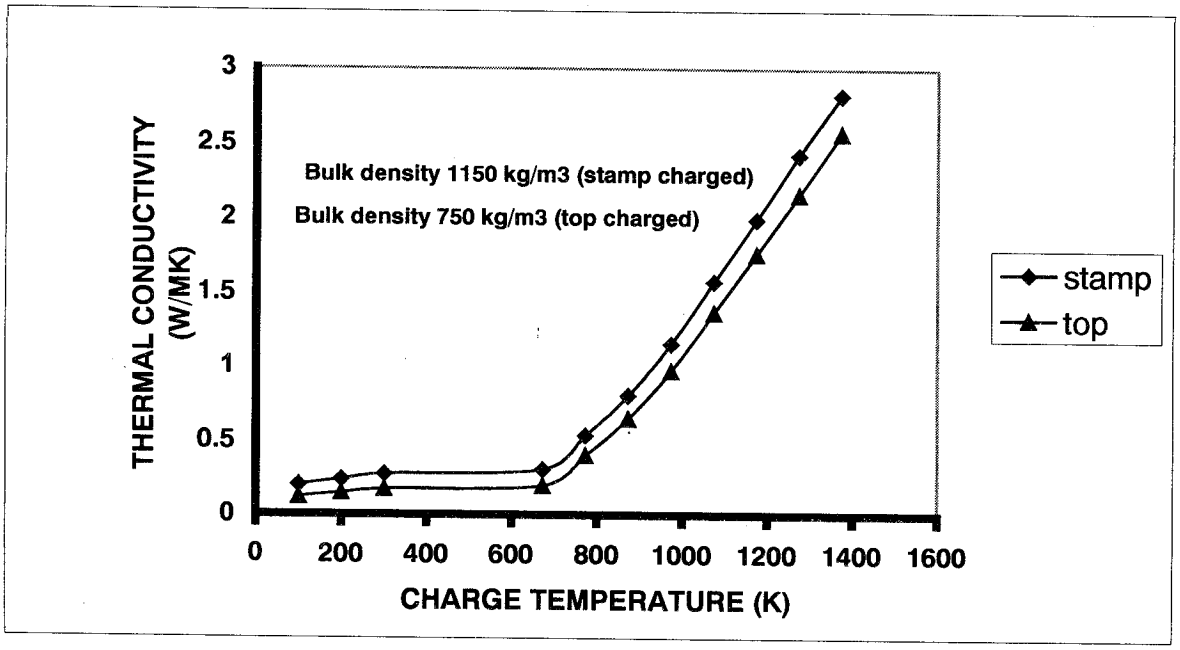

Fig 11: Comparison of thermal conductivity for stamp and top charged ovens

oven charge. Since no published data for bulk density variation of stamp charged oven is available, the comparison of the trend of bulk density variation as a function of charge temperature predicted by the present model for stamp charged oven is compared with that for the top charged oven as reported in the literature /7- 9/. The trends are found to be quite consistent. Figure 11 shows a comparison of the thermal conductivity variation of the charge as a function of charge (coking) temperature during carbonisation in stamp and top charged ovens with different bulk densities. Since the charge bulk density in the stamp charged oven is higher

than the top charge oven, the effective thermal conductivity of the same coal is found to be higher in the stamp-charged oven during full carbonisation cycle. This verifies that the approach is fundamentally consistent with the process phenomenology.

5. CONCLUSION

A series of models relating the physical properties of an oven charge to the changes in chemical composition has been developed. The models are based on the fundamental concepts and some published data and are constructed in conjunction with volatile matter evolution model. The model of volatile matter evolution predicts the yield and composition as a function of temperature from the ultimate analysis of the coal and the heating rate for a typical the coke oven. The model considers the evolution of the following species, primary volatile matter, methane, carbon monoxide and hydrogen. The evolution of these species is governed by parallel first order decomposition reactions, the rate constants for which depend on a distribution of activation energies. For prediction of the carbonisation heat of reaction a heat balance model relating the heat release at any stage of carbonisation to the cumulative yield of volatile matter species has been developed. The actual heat release occurs as the semi-coke matures. The carbonisation heat release does not occur until the semi-coke is converted to coke with the release of the volatile matter. Predictive models relating the thermo-physical properties of the oven charge in conjunction with the change in chemical composition and structural characteristics are also developed. These models provide mechanistic interpretation of the fundamental processes and published theoretical and experimental investigations. The main source of some deviations in some of the predictions is attributed to lack of availability of comprehensive database for Indian coals and variation of coal compositions with regard to geographical location. However, the results obtained from the mathematical model predictions are in good agreement and fairly consistent with those available in the published literature /6-9/ (deviations are less than 5%). The model-based code (*COKESIM-2*) can be a useful industrial tool for prediction of physical properties of coke oven charge during complete coking cycle.

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Nomenclature

$D(y)$	=	Debye function for specific heat
E(y)	=	Einstein function for specific heat
E	=	activation energy
E_0	=	starting activation energy
H	=	heat of combustion at 298 K
K and k	=	Thermal conductivities of the charge and constituents
$\overline{m_j}$	=	final yield of j^{th} volatile matter species
$m_0(t)$	=	mass of char remaining at time t
m_j	=	cumulative amount of j^{th} volatile matter species released at time t
N	=	number of volatile matter species
P_{jk}	=	coefficients derived from standard physical and chemical properties
q	=	heat release
R	=	universal gas constant
T	=	temperature
t	=	time
u_i	=	heat of formation of i^{th} volatile matter species
U_0	=	heat of formation of char
Y	=	yield of coke (per mass of initial charge)

Greek Symbols

y_i	=	mass fraction of C,H,O,N,S
κ	=	frequency factor
θ_D	=	characteristic Debye temperature
Θ_E	=	characteristic Einstein temperature
δ	=	fraction of component of volatile matter released
ε, β	=	coefficients which vary with species and coal rank

γ = bulk density of charge
γ_0 = initial bulk density of charge
Δv = fractional volume change
ϕ_I = constants representing heats of combustion
Δh = change in enthalpy from 298 k to T k
λ_I = constants (related to heat of combustion)
μ_I = atomic weights of C, H, O, N, S
ε = total charge porosity
ε_{int} = the fraction of the charge volume occupied by internal pores
ε_{ext} = the fraction of the charge volume occupied by the fissures and cracks.

6. REFERENCES

1. D. Merrick, *Fuel*, **62**, 534-539 (1983).
2. E.J. Osinski, P.V Barr and J.K Brimacombe, *Ironmaking and Steelmaking*, **20(5)**, 350-359 (1993).
3. E.J. Osinski, P.V. Barr and J.K. Brimacombe, *Ironmaking and Steelmaking*, **20(6)**, 453-467 (1993).
4. P.V. Barr, E.J. Osinski, J.K. Brimacombe, M.A. Khan and P.J. Readthough, *Ironmaking and Steelmaking*, **21(1)**, 44-55 (1994).
5. D.J. Millard, *J. Inst. Fuel*, **28**, 345-351 (1955).
6. D. Merrick, *ISS Iron-making Proc.*, **43**, 287-302 (1984).
7. D. Merrick, *Fuel*, **62**, 540-546 (1983).
8. D. Merrick, *Fuel*, **62**, 547-552 (1983).
9. D. Merrick, *Fuel*, **62**, 553-561 (1983).
10. V.R. Voller, M. Cross and D. Merrick, *Fuel*, **62**, 562-570 (1983).
11. E.J. Osinski, J.K. Brimacombe, P.V. Barr and M.A. Khan, Proc.2nd Int. "*Cokemaking*" Cong. , **2**, 374-396 (1992).
12. E.J. Osinski, J.K. Brimacombe, P.V. Barr, J.E. Grandsen and M.A. Khan, *ISS Ironmaking Proc.*, **51**, 421-433 (1992).
13. K.L. Chen and M.Q. Chin, *ISS Iron making Proc.*, **45**, 279-286 (1986).
14. G.C. Laurier, P.J. Readyhough and G.R. Sulivan, *Fuel*, **65**, 1190-1195 (1986).
15. A.M. Reilly, P.J. Readyhough and G.R. Sulivan, *Fuel*, **67**, 997-1002 (1988).
16. S.K.Das, K.M.Godiwalla, S.P.Mehrotra, Amit Chatterjee S.H.Krishnan and P.C.Choudhary, *High Temperature Materials and Processes*, **24(5)**, 301-314 (2005)